A Vibrational spectroscopic study of the mixed anion mineral sanjuanite $Al_2(PO_4)(SO_4)(OH)\cdot 9H_2O$

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ABSTRACT

The mineral sanjuanite $Al_2(PO_4)(SO_4)(OH)\cdot 9H_2O$ has been characterised by Raman spectroscopy complimented by infrared spectroscopy. The mineral is characterised by an intense Raman band at 984 cm^{-1}, assigned to the $(PO_4)^{3-}$ ν_1 symmetric stretching mode. A shoulder band at 1037 cm^{-1} is attributed to the $(SO_4)^{2-}$ ν_1 symmetric stretching mode. Two Raman bands observed at 1102 and 1148 cm^{-1} are assigned to $(PO_4)^{3-}$ and $(SO_4)^{2-}$ ν_3 antisymmetric stretching modes. Multiple bands provide evidence for the reduction in symmetry of both anions. This concept is supported by the multiple sulphate and phosphate bending modes. Raman spectroscopy shows that there are more than one non-equivalent water molecules in the sanjuanite structure. There is evidence that structural disorder exists, shown by the complex set of overlapping bands in the Raman and infrared spectra. At least two types of water are identified with different hydrogen bond strengths. The involvement of water in the sanjuanite structure is essential for the mineral stability.

KEYWORDS: Raman spectroscopy, phosphate, sulphate, sanjuanite, hotsonite, kribergite

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INTRODUCTION

The mineral sanjuanite $Al_2(PO_4)(SO_4)(OH)\cdot 9H_2O$ was named after its locality of origin Sierra Chica de Zonda, San Juan Province, Argentina. The mineral is triclinic with *a*= 11.34, *b*=9.018 and *c*=7.376 Å and with space group P1.[1] The mineral is a mixed anion compound and may be classified as a hydrated phosphate with additional ions under the Dana classification. The mineral belongs to the sanjuanite-destinezite group (destinezite - $Fe_2(PO_4)(SO_4)(OH)\cdot 6H_2O$), which also includes the mineral sarmienite ($Fe_2(AsO_4)(SO_4)(OH)\cdot 5H_2O$). The mineral is also related to another aluminium phosphate hotsonite ($Al_5(PO_4)(SO_4)(OH)_{10}\cdot 8H_2O$) at least by formula. This latter mineral is also named after its locality Hotson 42, about 65 km West of Pofadder, Bushmanland, Cape Province, South Africa. Another mineral related to sanjuanite is kribergite, $Al_5(PO_4)_3(SO_4)(OH)_4\cdot 4H_2O$, with a reported triclinic cell of *a*=18.126, *b*=13.519 and *c*=7.500 Å. [1] The minerals sanjuanite, hotsonite and kribergite are all suphate-phosphates of aluminium. Little crystallographic data exists on similar hydrated alumino phosphate–sulphates which tend to have similar morphologies. No data on the coordination of the PO_4 and SO_4 octahedra in these minerals is known. A detailed investigation into these minerals is required becasue any structural information is very limited. There are only four published works on sanjuanite,[1-4] none of which investigate the molecular structure of this mineral using vibrational spectroscopy techniques.

The mineral sanjuanite contains both sulphate and phosphate anions, and therefore, the presence of these anions can be observed using vibrational spectroscopy. A good starting point to study the position of the expected bands is to observe where the bands occur in aqueous solutions and then to observe the position of the bands resulting from the vibrational spectroscopy of minerals containing the individual anions. In aqueous systems, the sulphate anion is of T_d symmetry and has symmetric stretching mode (ν_1) at 981 cm^{-1}, the antisymmetric stretching mode (ν_3) at 1104 cm^{-1},the symmetric bending mode (ν_2) at 451 cm^{-1} and the ν_4 mode at 613 cm^{-1}. [5] Ross reported that sulfate fundamental and bending modes are observed at 1000 cm^{-1} (ν_1), 480 cm^{-1} (ν_2) , 1121, 1085 and 1068 cm^{-1} (ν_3), 645 and 600 cm^{-1} (ν_4). [6] The Raman spectrum of the mineral chalcanthite shows a single symmetric stretching mode at 984.7 cm^{-1}.[7] Two ν_2 modes are observed at 463 and 445 cm^{-1} and three ν_3 modes at 1173, 1146 and 1100 cm^{-1}. The ν_4 mode is observed as a single band at 610 cm^{-1}. In aqueous systems, Raman spectra of phosphate oxyanions show a symmetric stretching mode

(ν_1) at 938 cm^{-1}, the antisymmetric stretching mode (ν_3) at 1017 cm^{-1}, the symmetric bending mode (ν_2) at 420 cm^{-1} and the ν4 mode at 567 cm^{-1}. [5] The Raman spectroscopy of some phosphate minerals have been studied. These results serve to show the positions of the bands which may be assigned to sulphate and phosphate.

Raman spectroscopy has proven very useful for the study of minerals. Indeed Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with minerals containing sulphate and phosphate groups.[8-11] This paper is part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone. In this work we attribute bands at various wavenumbers to vibrational modes of sanjuanite using Raman spectroscopy and relate the spectra to the structure of the mineral. The mineral is distinguished from other cave minerals such as gypsum and calcite through its Raman spectrum.

EXPERIMENTAL

Mineral

The mineral sanjuanite $Al_2(PO_4)(SO_4)(OH)\cdot 9H_2O$ used in this research originated from Chica de Zonda, San Juan Province, Argentina. The mineral was obtained from the Mineralogical Research Company.

Raman spectroscopy

Crystals of sanjuanite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarised light at 633 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of ± 1 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition on the crystals using the highest magnification (50x) were accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

Band component analysis was undertaken using the Jandel 'Peakfit' (Erkrath, Germany) software package which enabled the type of fitting function to be selected and allowed specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Lorentz-Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations (r^2) greater than 0.995. Band fitting of the spectra is quite reliable providing there is some band separation or changes in the spectral profile.

RESULTS AND DISCUSSION

The mineral sanjuanite contains four vibrational spectroscopically distinct units, namely phosphate, sulphate and hydroxyl units as well as water. Each one of these species has its own characteristic spectrum which is generally separate from the spectrum of other units. Some overlap of bands is expected.

There is a complex series of weak Raman bands at 3575, 3509, 3406, 3330, 3152, and 3090 cm^{-1}, Fig. 1a. OH has only one stretching vibration (ν_{OH}) located at around 3570 cm^{-1}. The first order H-O-H bending overtones and H-O-H stretching fundamentals, for H_2O bearing minerals generally occur in the 3450-3200 cm^{-1} region. The H-O-H bending region for these types of minerals is around 1670 cm^{-1} [12]. Therefore, the higher wavenumber bands (3575 and 3509 cm^{-1}) are assigned to OH stretching vibrations of water (ν_3), while the bands at lower wavenumbers (3406 and 3330 cm^{-1}) are assigned to the ν_1 modes. The H-O-H bending bands associated with these bands are not observed. This is not unexpected as water is a very weak Raman scatterer. The bands at around 3152 and 3090 cm^{-1} are attributed to water which is strongly hydrogen bonded to the sulfate and phosphate anions. Raman spectroscopy shows that there are more than one non-equivalent water molecules in the sanjuanite structure.

The infrared spectra of sanjuanite are provided in the Supplementary Information. The infrared spectrum of the hydroxyl stretching region of sanjuanite is reported in Fig. 1b. The spectrum is complex with a series of overlapping bands. Shoulders are observed in the spectral profile and these shoulders determine the position of the component bands. Infrared bands are observed at 2917, 2978, 3131, 3350, 3486, 3576 cm^{-1}. The band at 3576 cm^{-1} is assigned to the OH stretching vibration of the hydroxyl units. These other bands are assigned to water stretching vibrations. The bands at the lower wavenumbers at 2917, 2978, and 3131 cm^{-1} are attributed to strongly hydrogen bonded water and correspond with the water bending vibration at 1675 cm^{-1}. The higher wavenumber bands are associated with weakly hydrogen bonded water molecules.

The Raman spectrum of sanjuanite in the 900 to 1500 cm^{-1} range is displayed in Fig. 2a. Two low intensity overlapping bands are found at 1457 and 1438 cm^{-1}. The assignment of these bands is not easy; however the same bands are observed as weak bands in the infrared spectrum (Fig. 2b). Here low intensity infrared bands are found at 1460 and 1545 cm^{-1}. Two intense infrared bands are observed at 1627 and 1675 cm^{-1}. These bands are attributed to weakly hydrogen and strongly hydrogen bonded water. This observation is important as it means there are two types of water in the sanjuanite structure and their presence is required for the stability of the mineral.

The Raman spectrum is dominated by the intense bands at 984 cm^{-1} assigned to the $(PO_4)^{3-}$ ν_1 symmetric stretching band. A shoulder observed at 1037 cm^{-1} is assigned to the $(SO_4)^{2-}$ ν_1 symmetric stretching mode. It is probable that there is coupling between the sulphate and phosphate stretching modes resulting in the intense band at 984 cm^{-1}. The other low intensity bands at 1102 and 1148 cm^{-1} are attributed to the ν_3 antisymmetric stretching modes of the $(PO_4)^{3-}$ and $(SO_4)^{2-}$ units. The fact that multiple antisymmetric stretching modes are observed provides evidence for the reduction of symmetry of the sulphate anion in the sanjuanite structure. Some sulphates have their symmetry reduced through acting as monodentate and bidentate ligands. In the case of bidentate behaviour both bridging and chelating ligands are known. This reduction in symmetry is observed by the splitting of the ν_3 and ν_4 into two components under C_{3v} symmetry and 3 components under C_{2v} symmetry.

The Raman spectrum of sanjuanite in the 300 to 700 cm^{-1} region is shown in Fig. 3a. The spectral profile consists of an intense band at 609 cm^{-1} assigned to the $\nu_4 (SO_4)^{2-}$ bending mode. The band at 523 cm^{-1} is ascribed to the $\nu_4 (PO_4)^{3-}$ bending mode. Fig. 3b displays the infrared spectrum in the 750 to 1250 cm^{-1} range. Two infrared bands are observed at 849 and 882 cm^{-1}. These bands are not observed in the Raman spectrum. The bands are attributed to an out of line chain vibration of Al-O-P units. The fact that it is observed in the Infrared spectrum and not the Raman spectrum suggests that the band is due to an anitsymmetric vibration. A series of overlapping bands are observed at 981 (sharp), 1020, 1056, 1096, 1144 and 1181 cm^{-1}. The sharp band at 981 cm^{-1} is assigned to the infrared activated $(PO_4)^{3-}$ ν_1 symmetric stretching band. The shoulder at 1020 cm^{-1} is assigned to the $(SO_4)^{2-}$ ν_1 symmetric stretching mode. The assignment of the remaining four bands is difficult. One possibility is that the first two bands are due to the $(PO_4)^{3-}$ ν_3 antisymmetric stretching modes and the latter two to the $(SO_4)^{2-}$ ν_3 antisymmetric stretching modes. Whether this attribution is correct or not is open to question, as there is the likelihood of mixing of vibrational modes.

The low wavenumber region of the Raman spectrum of sanjuanite is shown in Fig. 4a. Raman bands are observed at 108, 142 with a shoulder at 152, 184, 197 and 218 cm^{-1}. It is considered that these bands in this spectral region are associated with water hydrogen bonded to the sulphate and phosphate anions and to lattice vibrations. The intense band at 142 cm^{-1} is considered to be due to hydrogen bond formation.

The infrared spectrum of sanjuanite in the 500 to 750 cm^{-1} region is reported in Fig. 4b. Four infrared bands are observed at 576, 587, 629 and 657 cm^{-1}. In harmony with the assignment of the Raman bands, the two bands at 576 and 587 cm^{-1} are assigned to the $\nu_4 (F_2)$ $(PO_4)^{3-}$ bending modes and the two bands at 629 and 657 cm^{-1} are attributed to the $\nu_4 (F_2)$ $(SO_4)^{2-}$ bending modes. In the infrared spectrum, it could be expected to find water librational mode(s). It is possible that the intense infrared band at 657 cm^{-1} is such a vibration.

Intense Raman bands are found at 466 and 430 cm^{-1} with a smaller intensity band at 400 cm^{-1}. These bands are attributed to the $\nu_2 (SO_4)^{2-}$ bending modes. The series of Raman bands at 365, 351, and 337 cm^{-1} are associated to the $\nu_2 (PO_4)^{3-}$ bending modes. The infrared range in Fig. 4b, is limited by the infrared technique itself as the cell totally adsorbs the infrared radiation below 550 cm^{-1}.

CONCLUSIONS

Raman complimented with infrared spectroscopy has been used to characterise the mineral sanjuanite. The mineral is an unusual mineral from a chemistry point of view as the mineral contains both phosphate and sulphate anions. Only two other minerals, hotsonite and kribergite, has the same chemistry. The structures of all of these minerals are unknown and Raman spectroscopy enables information at the molecular level to be obtained. The Raman and infrared spectra reflect the composition of the mineral with bands attributed to H_2O, PO_4 and SO_4 stretching and bending modes. At least two types of water are identified in the structure of sanjuanite namely weakly and very strongly hydrogen bonded water molecules.

Acknowledgements

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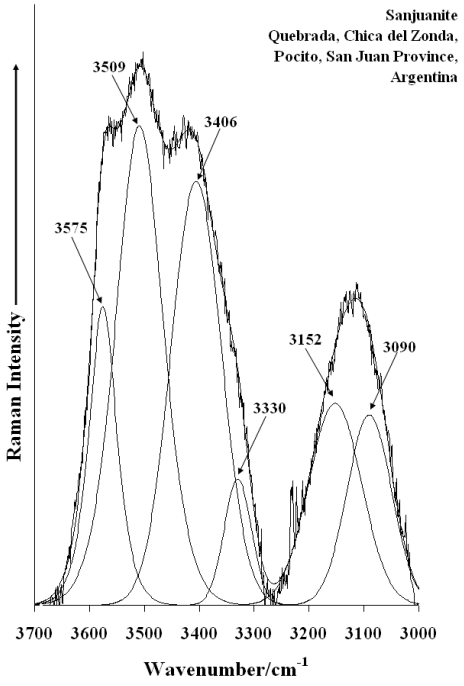

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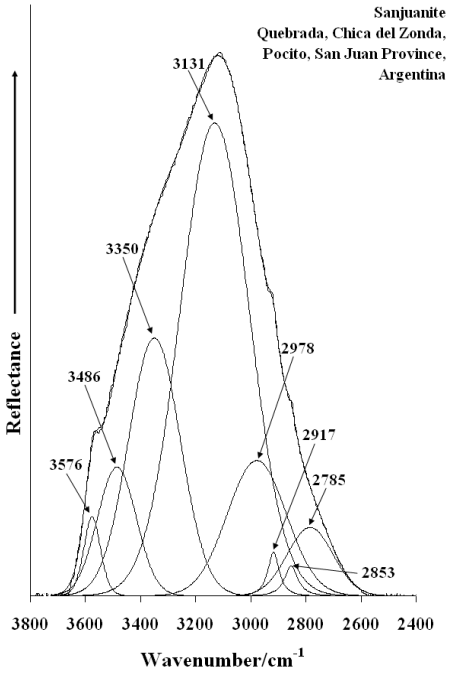

Figure 1b

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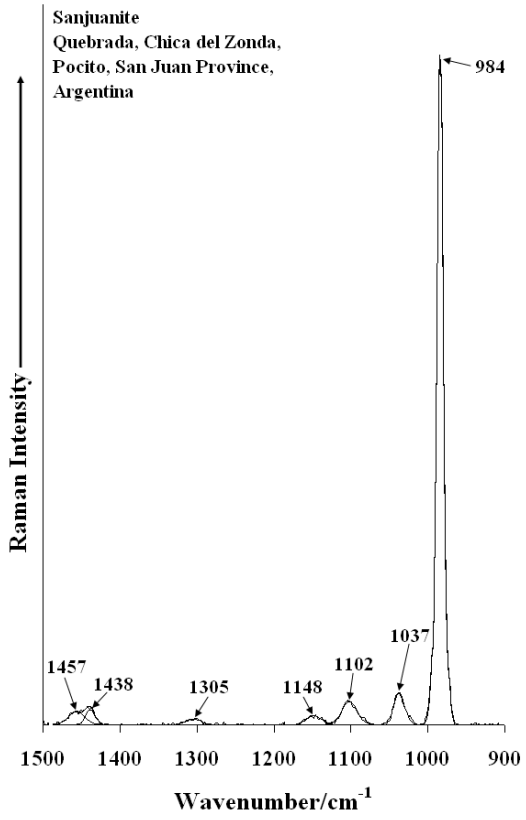

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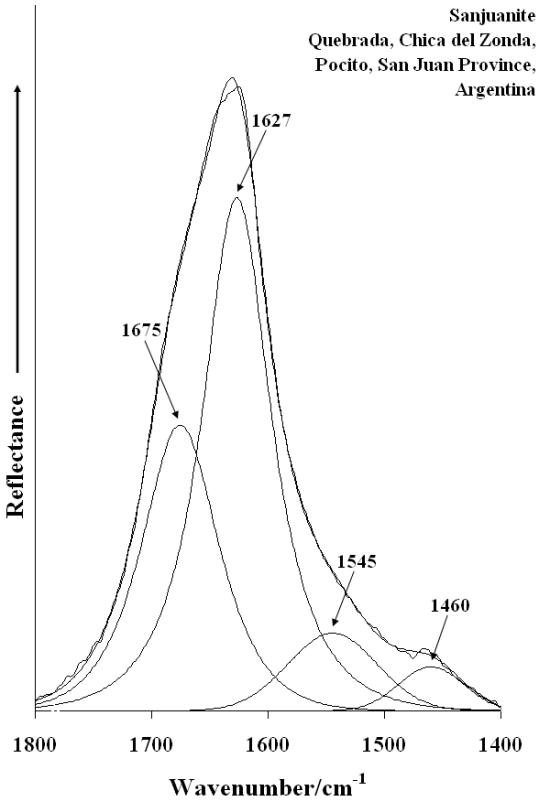

Figure 2b

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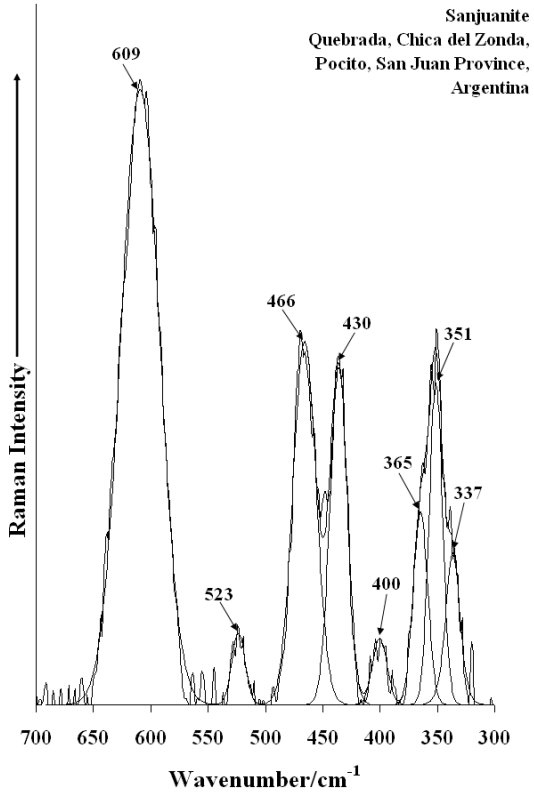

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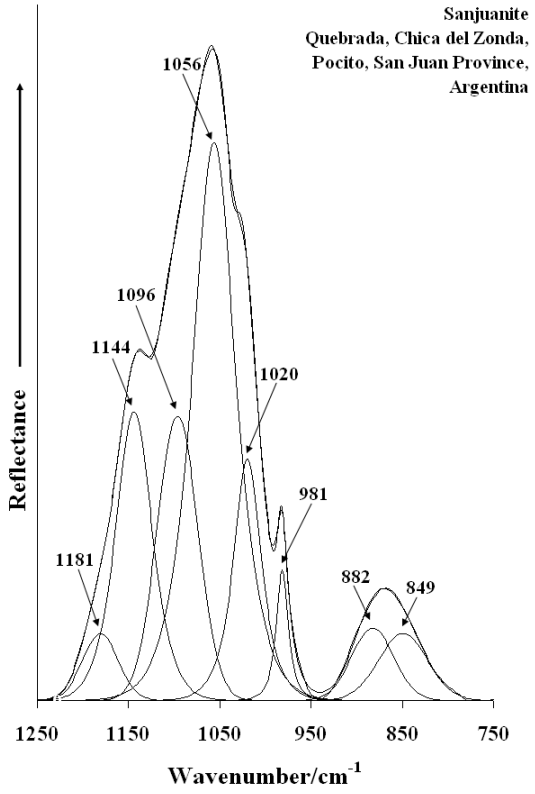

Figure 3b

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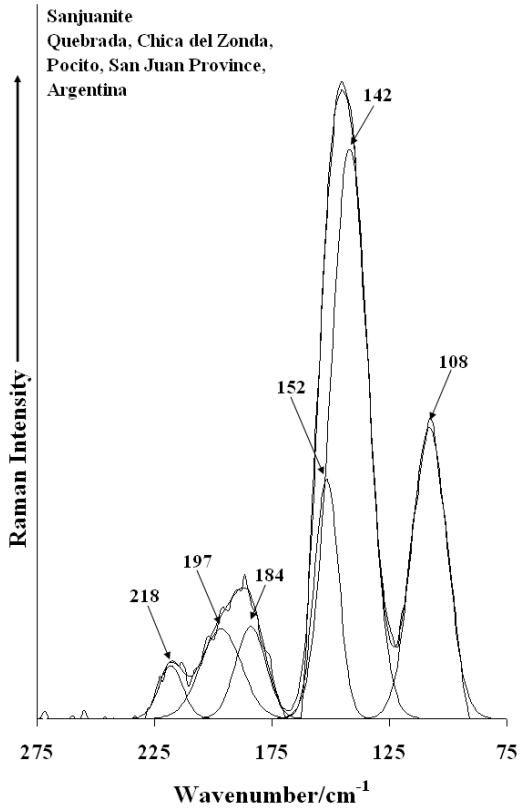

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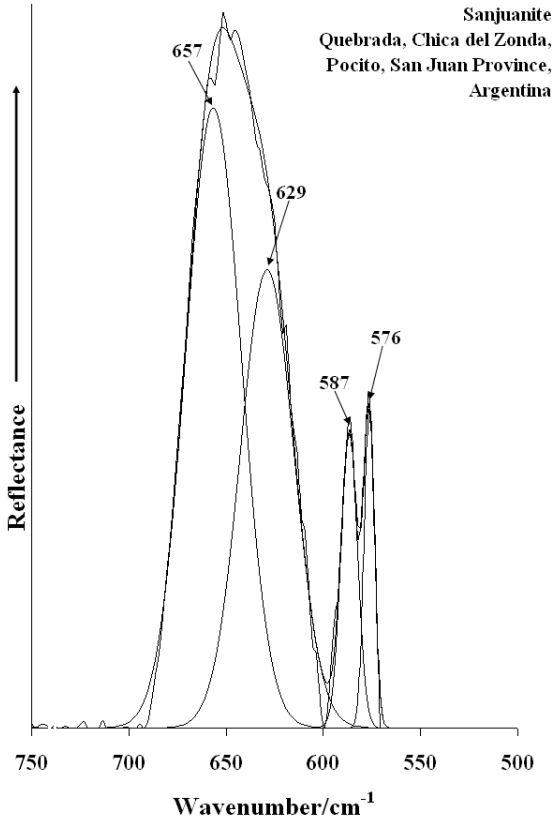

Figure 4b

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